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NEXT-GENERATION FIRE EXTINGUISHING AGENT, PHASE I - SUPPRESSION CONCEPTS

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This report documents Phase I of an effort to develop concepts for new and more effective fire extinguishing agents. In Phase I a technology review was performed, suppression hypotheses were developed, and a Phase II plan was established. The technology review covers fire physics, chemistry, and engineering information relevant to flame structure, fire modeling, combustion reactions, oxidation kinetics, and fire suppression. The Phase II effort will emphasize halon-like agents owing to their cleanliness and ability to suppress three-dimensional fires.

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PREFACE

This report has been reviewed by the Public Affairs Officer (PA) and is releasable to the National Techincal Information Service (NTIS). At NTIS it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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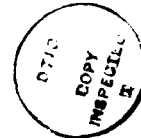
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TABLE OF CONTENTS

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SECTION I

INTRODUCTION

A. OBJECTIVE

The objective of this effort was to originate concepts for a next-generation suppressant for multidimensional fires. A complete analyses of the molecular basis for the agent action and of the quantitative burning inhibition was obtained.

B. BACKGROUND

Although many new types of fire suppressants have been developed, improved agents are still needed. The fires of primary interest are Class B (liquid fuel) fires. Three types of agents are used by the Air Force and Navy for Class B fires (Reference 1). Foams, such as aqueous film-forming foam (AFFF), have low toxicities and provide excellent security against flashback and burnback of liquid fuels: however, foams are not three-dimensional and are dirty. Solid agents, such as potassium bicarbonate ($KHCO_3$), are excellent suppressants against liquid fuel fires; however, they too are dirty, have very poor deliverability, and give only moderate security. Halons have excellent dimensionality (they are highly effective against flowing liquid fuel fires) and they are clean; however, they give poor security and have poor deliverability, particularly outdoors with adverse winds. Moreover, many halons have serious toxicity problems and potentially unacceptable environmental impacts. Advanced knowledge in combustion physics, molecular dynamics, and theoretical chemistry gives reason to believe that a search for new and more effective agents can be successful.

1

C. SCOPE

The scope of this task involves the origination of concepts for new and more effective types of fire extinguishants based on current knowledge of the chemistry and physics of combustion processes. The concepts may involve any combination of inhibitors which act by chemical and/or physical mechanisms or by new modes of utilization. Hypotheses will be tested using laboratory-scale experiments. Fire parameters will be monitored throughout the testing to provide information concerning mechanisms of action and to permit feedback for refinement of original concepts and origination of new concepts. Sufficient research to determine the molecular mechanisms of extinguishment of selected agents will also be performed. The next-generation agent(s) should be able to suppress one-, two-, or three-dimensional fires with minimal application under a range of ambient conditions. The final product of this project will be a technical report detailing all work accomplished, with conclusions and recommendations.

D. TECHNICAL APPROACH

The following tasks were required for Phase I of this project. A comprehensive search was conducted to acquire and analyze fire physics, chemistry, and engineering information relevant to flame structure, fire modeling, combustion reactions, oxidation kinetics, combustion thermodynamics, and fire suppression. Emphasis was placed on known and possible mechanisms of fire extinguishment and on known fire-inhibiting agents. From the information acquired, new mechanisms which offer potential for fire suppression were hypothesized. New agents, based on both known and hypothetical fire suppression mechanisms, were then proposed. Among the concepts considered are those agents that operate primarily by physical modes, agents whose actions are chemically dependent, new methods of introduction and utilization (e.g., encapsulation or compositive foams),and combinations of these concepts. Of special importance were agents whose fire suppression mechanism involved recycled reactive species and branched reactions.

2

SECTION II
COMBUSTION

Combustion is an oxidation/reduction reaction sufficiently intense to give off heat and visible light. Fire is uncontrolled combustion. In oxidation/reduction reactions, a reducing agent gives up electrons to an oxidizing agent. The oxidizing agent for nearly all fires encountered by the firefighter is oxygen from the air. In unusual cases the oxidizing agent may be pure oxygen, hydrogen peroxide, organic peroxides, ozone, metal peroxides, dinitrogen tetroxide, or other oxidants. Some of these unusual oxidizing agents are encountered in propulsion systems for space vehicles. The reducing agents for typical fires are cellulosic materials (paper, wood), which give Class A fires; liquid fuels (gasoline, alcohol, hydrazine, JP-4, JP-5, JP-8, petroleum), which give Class B fires; and metals (magnesium, lithium, sodium, titanium), which give Class D fires. Class C fires involve live electrical components in the fire. In some cases (explosives, for example) the oxidizing agent and the reducing agent are combined in the same material or even in the same molecule. Fires involving such materials are exceedingly difficult to extinguish and require special procedures. In general, this project involves extinguishment of Class B fires with some interest in Class A, C, and D fires. Of primary concern are diffusion fires where the oxidizing agent is air.

Fires can be examined from either a macroscopic (diffusion, radiation, transport) or a microscopic (free radicals, pathways, kinetics) standpoint. The first standpoint is often considered the realm of the engineer, while the second is the realm of the chemist. The following attempts to combine these two treatments. A fundamental understanding of fire characteristics (Reference 2) is necessary for the establishment of proper extinguishment techniques.

Fire is caused by chemical reactions. Thermodynamics determines whether a reaction can go (i.e., whether a reaction is spontaneous);

kinetics determines whether a reaction goes with sufficient speed to be of importance. As a general rule of thumb, exothermic (heat-releasing) reactions are spontaneous; endothermic (heat-absorbing) reactions are not.[*] Since all (or nearly all) oxidation reactions of normal fuels (JP-4, wood, metal, etc.) are exothermic, such reactions are spontaneous. Fortunately, owing to chemical kinetics, not all such reactions proceed with sufficiently high velocities to be important. Most combustion reactions are kinetically controlled rather than thermodynamically controlled. This differentiation is seen below.

Before a spontaneous oxidation/reduction reaction (or, in general, any spontaneous reaction) can occur, sufficient energy must be available to initiate and sustain the reaction. This initiation energy is termed the "activation energy." If if were not for the activation energy, all thermodynamically possible reactions would continue to completion. Weapons, facilities, and aircraft would burn spontaneously in the air in which they are immersed (Reference 3). But activation energy makes it possible for fuel and oxidizing agent to exist side by side, for firefighters to operate, and for the world to exist as something other than a mixture of combustion products. For example, the activation energy for the direct reaction of hydrocarbons with diatomic oxygen is very high. For this reason, JP-4 and air or (for simplicity) methane and air can coexist with no combustion taking place (Equation (1)).

$$
\begin{array}{c}
\text{H} \\
| \\
\text{H-C-H} \quad + \quad \text{O=O} \quad \rightarrow \quad \text{no reaction under ordinary conditions} \\
| \\
\text{H}
\end{array} \qquad (1)
$$

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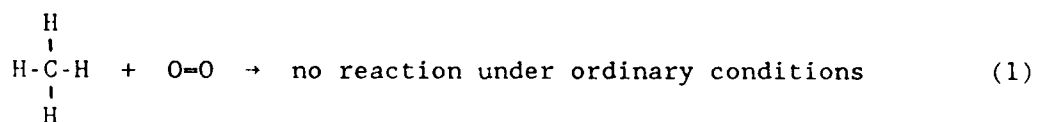
*Exothermic reactions have negative reaction enthalpies (ΔH values). Endothermic reactions have positive reaction enthalpies.

This reaction is unimportant under normal ambient conditions. Carbon-hydrogen and oxygen-oxygen bond strengths are very high and molecular collisions between molecules containing such bonds are unlikely to be sufficiently energetic at ordinary temperatures to cause reaction. The energy required to effect bond-breaking and initiate reaction is the activation energy.

At higher temperatures, where the activation energy is supplied, a number of things can happen. First, the collision energy between, e.g., methane and oxygen molecules may be sufficiently energetic to cause bond rupture and initiate reaction as shown in Equation (2).

$$
\begin{array}{cccccccc}
& H & & & & H & & \\
& | & & & & | & & \\
H-C-H & + & O\!=\!O & \rightarrow & H-C & + & H-O-O & \qquad(2)\\
& | & & & & | & & \\
& H & & & & H & &
\end{array}
$$
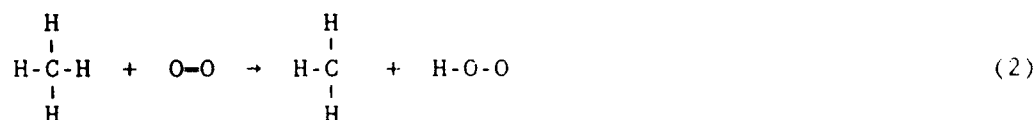
This reaction has not directly produced carbon dioxide and water, which are the final products of the complete combustion of methane. This point is discussed below.

A second reaction that can initiate the reaction of methane with oxygen at higher temperatures is pyrolysis (thermal decomposition).

$$
\begin{array}{cccccccc}
& H & & & & H & & \\
& | & & & & | & & \\
H-C-H & + & heat & \rightarrow & H-C & + & H & \qquad(3)\\
& | & & & & | & & \\
& H & & & & H & &
\end{array}
$$

Pyrolysis occurs from to high-energy molecular collisions with other molecules of the same type, other types (nitrogen, oxygen, argon), or container walls. Thus, Equation (3) is not complete as shown; however, pyrolysis reactions are often written as if they were simple and unimolecular (one-molecule). Note that in this reaction, oxygen has not appeared at all; however, bond breakage has occurred so that further

reaction with oxygen becomes very easy. Other initiation mechanisms are also possible.

Once reaction is initiated, the activation energy is continuously supplied by the heat output of the fire itself. A large part of this supplied energy is due to the fire radiation field. To a considerable extent, fires are self-sustaining. In addition to the continuous supply of activation energy, there is a more important reason why combustion usually continues once it is initiated. Reactions with very high activation energies (e.g., Equation (1)) are replaced by free-radical reactions which have much lower activation energies. For example, for the two species shown in Equation (1) to react, at least two different bonds must be broken. These are a carbon-hydrogen bond and, depending on the products, at least one of the two oxygen-oxygen bonds in double-bonded diatomic oxygen. On the other hand, a hydrogen atom, such as that formed in Equation (3), can react with an oxygen molecule by breaking only one bond and simultaneously forming a second (Equation (4)).

$$H + O=O \rightarrow H-O + O \qquad (4)$$

Such reactions, which have low activation energies, are very fast, even at lower temperatures.

Free-radical reactions involve high-energy species (free radicals) formed by disruption of normally stable molecules. Since part of the necessary energy for reaction has already been supplied, such radicals react with very low activation energies. In fact, one way to initiate a combustion reaction is to supply a few free radicals. A mixture of hydrogen and oxygen is stable until irradiated with UV light, which causes bond breaking and formation of a few hydrogen-free radicals (hydrogen atoms) to start the combustion process. Similarly, mixtures of hydrocarbons with air are more susceptible to combustion initiation by a burning match (whose flame supplies free radicals) than by a hot surface.

6

Thus, fires not only contain radiation fields to supply activation energy to molecules and to evaporate fuel for combustion, they also contain free-radical pools. Indeed, the principal reactants within fires are free radicals. Even the very simple reaction between methane and diatomic oxygen to form water and carbon dioxide cannot occur as shown by the balanced equation

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (5)$$

This is true for three reasons. First, simultaneous collisions between three molecules, as implied by this reaction, are unlikely to occur. Most actual reactions are bimolecular; they involve collisions of two reacting species. Second, even if trimolecular collisions were common, only at very high temperatures would reactions such as implied in Equation (5) occur owing to the very high activation energy required to break a number of bonds. Bonds are usually broken one at a time. Third, the atom rearrangements necessary for the relatively complex reactants to form equally complex products are complicated and unlikely to occur as a uniform and continuous process. Any reaction involving complicated molecules nearly always occurs as a series of simpler reactions. For combustion reactions, these are nearly all bimolecular (two-molecule) free-radical reaction steps.

Much study has been devoted to elucidation of the various free-radical reactions and their roles in combustion (Reference 4). The number of different free-radical reactions possible for even simple hydrocarbons is immense. At least 25 species and over 300 simple reactions must be considered to fully describe the combustion of methane (Reference 5). Higher-molecular weight fuels, whose molecules are more complex, require even more reactions to describe their combustion (Reference 6). The earlier work on hydrocarbon combustion emphasized reactions in which oxygen and free-radical oxygen-containing species (O, OH, HO_2) played dominant roles (References 7 and 8). The abstraction of hydrogen atoms from hydrocarbons by OH (Equation (6)) is believed by some to be the principal mechanism of

fuel consumption in lean and stoichiometric hydrocarbon/air flames
(Reference 9).

$$R-H + OH \rightarrow R + H_2O \tag{6}$$

On the other hand, recent work has emphasized the roles of hydrogen atoms in
hydrocarbon combustion. It is generally accepted that for methane, hydrogen
atom abstraction (Equation (7)) is the principal reaction which initiates
the combustion chain leading to complete oxidation (Reference 10).

$$CH_4 + H \rightarrow CH_3 + H_2 \tag{7}$$

For some cases of methane combustion, 60 percent of methane removal and 98
percent of oxygen disappearance is due to reaction with hydrogen atoms
(Reference 11).

The important role of the hydrogen atom in hydrocarbon combustion is
substantiated by considerable evidence. A survey of experimental studies
indicates that, along with the reaction described by Equation (7), the
following series of reactions is not unreasonable for the primary free-
radical reactions involved in the combustion of methane.

$$CH_3 + O \rightarrow CH_2O + H \tag{8}$$

$$CH_2O + H \rightarrow CHO + H_2 \tag{9}$$

$$CHO + H \rightarrow CO + H_2 \tag{10}$$

$$CO + OH \rightarrow CO_2 + H \tag{11}$$

The diatomic hydrogen then reacts with oxygen and hydroxyl free radicals to
give monoatomic hydrogen.

$$H_2 + O \rightarrow OH + H \tag{12}$$

8

$$H_2 + OH \rightarrow H_2O + H \tag{13}$$

These simple bimolecular reactions rapidly increase in number as combustion proceeds owing to chain-branching processes, which increase the number of free-radical species. For hydrocarbon combustion, some chain-branching reactions (Reference 12) are those given in Equations (4), (12), and (14).

$$CH_4 + O \rightarrow CH_3 + OH \tag{14}$$

Fires may be either premixed (oxygen or air is mixed with the fuel prior to combustion) or diffusion (oxygen or air diffuses into the flame as combustion occurs). Nearly all fires of interest in fire protection are diffusion. In the limit, diffusion flames may be buoyancy-driven or momentum-driven (Reference 13). In momentum-driven flames the mass imbalance, owing to fuel introduction, causes movement and mixing of fuel and air. In buoyancy-driven flames the buoyancy of the hot gas effects mixing. All fires of interest here are buoyancy-driven, often with wind providing an additional driving force.

Liquids (and most solids) burn in the gas phase owing to vapor release. The condensed phase fuel vaporizes from the surface and moves to the flame front where it meets oxygen moving in from the surroundings. The rate, r, at which burning occurs for condensed phases is proportional to the rate of heat transfer, q, from the flame front to the fuel surface and inversely proportional to the heat, H, required for heating and evaporating the fuel.

$$r - k(q/H) \tag{15}$$

Chemical processes are assumed to occur so rapidly that the rate of combustion for condensed fuels is determined solely by mass and heat transfer rates (Reference 14). Heat transfer to the fuel surface occurs owing to radiation, q_r, and thermal conduction, $\lambda(dT/dz)$, where λ is the thermal conductivity and dT/dz is the temperature gradient.

9

$$q = \lambda(dT/dz) + q_r \qquad\qquad (16)$$

For large pool fires, the primary source of heat transfer to the surface appears to be radiation. For small fires, with lower axial velocity components, conduction may be more important.

The equivalence ratio, ϕ, is defined as the fuel/oxidizer ratio divided by the stoichiometric fuel/oxidizer ratio. The conditions $\phi > 1$, $\phi = 1$, and $\phi < 1$ correspond to fuel-rich, stoichiometric, and fuel-lean systems. Just above the fuel surface and below the flame front, $\phi > 1$. At the flame front a stoichiometric mixture has been achieved, and $\phi = 1$. Behind the flame front where fuel is depleted and more air is entrained, $\phi < 1$.

SECTION III
EXTINGUISHMENT MECHANISMS

A. PHYSICAL AND CHEMICAL EXTINGUISHMENT

Four things are necessary for combustion.

1. Fuel (hydrocarbons, cellulosic materials, metals, etc.).
2. Oxidizer (usually air).
3. Heat, to effect fuel vaporization and to supply activation energy.
4. Free-radical chain reactions.

These four components of a fire form the fire tetrahedron. If any component is removed (or inhibited), the fire is extinguished. Based on this simple picture, seven basic methods have been used for fire suppression (Reference 15).

1. Isolate the fuel.
2. Isolate the oxidizer.
3. Cool the condensed phase.
4. Cool the gas phase.
5. Blow away the flame.
6. Inhibit the chemical reaction, homogeneously.
7. Inhibit the chemical reaction, heterogeneously.

Extinguishment mechanisms are divided into two types -- physical and chemical. It is sometimes difficult to describe a particular extinguishment method as belonging entirely to one class or another; however, methods 1-5 above are generally considered physical and methods 6 and 7 are considered chemical.

A number of physical extinguishment methods exist. Smothering isolates the fuel from the oxidizing agent. Foams effect this separation; however, their overall mode of action is more complicated. A fuel may be isolated by

11

creation of backfires or by pumping liquid fuels from a burning tank to another vessel. Air can be removed by displacement with an inert gas.

Cooling, another physical extinguishment mechanism, can be effected by the addition of materials with large heats of phase transition or large heat capacities. Water is an excellent example of such a material. Simple dilution can also lower the flame temperature to the point that combustion cannot be sustained.

Blowing away a flame separates the free-radical zone from the fuel, effectively terminating the free-radical chain reaction. Extinguishment by shock waves and sound arises from this action.

Chemical means of extinguishment are discussed in detail in the following section. Most of these methods depend on termination or suppression of one or more reactions within the free-radical chain. A large number of compounds are known to exhibit homogeneous or heterogeneous flame inhibition (Reference 16).

B. FUEL INERTION

Fuel inertion is not an extinguishment method; however, it is a method for securing an area once extinguishment is effected. The term "fuel inertion" is often a misnomer. Most fuel inertion methods increase the resistance to burnback, ignition, and flashback but do not give a fuel that is truly inert to combustion (Reference 17).

Solidification or gelling of fuel has been used to increase security. This technique reduces the fire hazard by reducing the fuel evaporation rate and decreasing the spread and dispersion of liquid fuels. Thickened fuels have been investigated as a means of decreasing the fire risk in aircraft ground crashes (References 18, 19, and 20). Reduction of the fuel

evaporation rate decreases the burn rate. Sodium soaps and amine-isocyanates give rapid gelling and large decreases in burn rates (Reference 21). Emulsification also reduces fuel fire hazards (Reference 22).

To date, no highly effective, safe, and clean fuel-inerting agent has been developed. Those agents which rely on fuel thickening are difficult to apply and almost invariably cause cleaning problems. The report (References 23, and 24) of a gelling agent based on a reaction between amines and carbon dioxide looks promising; however, efficacy must yet be shown. A major problem in the inerting of hydrocarbons is the low reactivities of such fuels. Although they ignite and burn readily, hydrocarbons do not react easily to form new inerted compounds.

SECTION IV
EXTINGUISHING AGENTS

A. INERT GASES

Nitrogen, argon, carbon dioxide, and other inert gases function as extinguishing agents by dilution of air. This mechanism is inefficient and most inert gases are relatively poor agents. Carbon dioxide exhibits a second mode of action -- cooling. In part, this cooling is because, carbon dioxide is cold when ejected. More important, carbon dioxide appears to react endothermically with particulate carbon.

$$CO_2(g) + C(s) \rightarrow 2CO(g), \quad \Delta H_{298} = +41.22 \text{ kcal/mol} \quad (17)$$
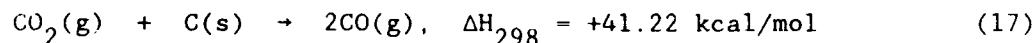
At room temperature this reaction is not spontaneous, but it becomes so at temperatures of 1000 $^\circ$C and above (Reference 25). The disappearance of carbon particles is evident from the color change of flames when carbon dioxide is used on a fire. While the overall reaction is undoubtedly that shown above, the actual pathway probably involves the two reactions below.

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g) \quad (18)$$

$$H_2O(g) + C(s) \rightarrow CO(g) + H_2(g) \quad (19)$$
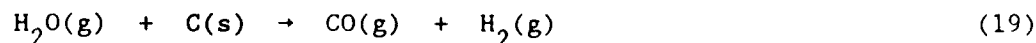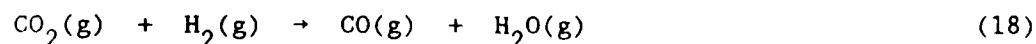
The removal of carbon particles also affects the fire by removing a major source of radiation back to a vaporizing fuel surface.

B. WATER

Water is highly effective against Class A fires, but it is only moderately successful against Class B fires, and then only when delivered as a fog or spray. Sprays cause delivery problems, and water is not an effective securing agent. The addition to water of certain materials --

detergents, thickening agents, and salts -- can give an improved
extinguishing agent for some fires; however, the agent is then di :y.

C.   FOAM

A variety of foams have been extensively and successfully used against
liquid-fuel fires. Two general classes of foams are protein-based and
synthetic. Each of these classes contains a large number of modifications.
Fluoroprotein foams contain a fluorinated surfactant. Polar-solvent foams
are effective against flammable polar liquids, which are destructive to many
foams. Low-expansion foams have expansion ratios between 4:1 and 8:1,
depending on the nozzle, while high-expansion foams have expansion ratios of
up to 1000:1. Low- and high-expansion foams are chemically similar; the
variation in expansion is primarily due to the foam-generation method. The
concentrations can be varied; however, most foam concentrates are prepared
to be mixed either 3 percent or 6 percent with water. A solid foam agent,
to be mixed with water before use, gives inconsistent fire extinguishment
and burnback resistance (Reference 26).

Foams cover the surfaces of burning fuels and seal them off from the
emission of the flame front. Foams separate the fuel from oxygen, and the
low-expansion foams provide significant cooling. Displacement of oxygen by
flash evaporation of water is a significant extinguishment mechanism
(Reference 27). Among the standard agents, foams provide the best security
against burnback.

Foams, however, suffer from two drawbacks. First, they are not clean
agents and require extensive cleanup after use. Second, foams lack three-
dimensionality.

D.   DRY CHEMICALS

Dry chemical agents, applied as powders, are heterogeneous fire
extinguishants. Such agents come in a variety of types. Bicarbonates and

ammonium salts are among the most effective of the dry chemical agents. Two possible modes of action of such compounds are heterogeneous removal of reactive species by combination on particle surfaces and homogeneous inhibition (Reference 28). Deactivation of reactive radical species by combination on surfaces resembles the extinguishment mechanism of halons (see below) in that a pathway is provided for combination. The pathway provided by dry chemicals is catalytic; that provided by halons is chemical. A homogeneous mechanism provided by particle vaporization may also play an important role in suppression by dry chemical agents (References 29, and 30). One possible homogeneous reaction is effected by the formation of potassium hydroxide, KOH, in thermal decomposition of potassium salts. The potassium hydroxide may scavenge hydrogen atoms (References 31, and 32).

$$KOH(g) + H(g) \rightarrow K(g) + H_2O(g) \tag{20}$$
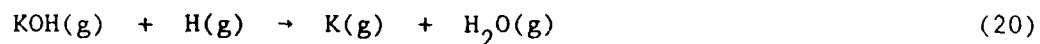
Sublimable inorganic halides such as aluminum chloride (Reference 33) may effect hydrogen recombination in a reaction similar to that of the halons. Carbon dioxide generation by thermal decomposition is apparently unimportant in the extinguishment capabilities of the bicarbonate dry-chemical agents.

Dry chemical agents provide outstanding extinguishment; they are often more effective than the halons. Three attributes, however, make them unacceptable for use by the Air Force or the Navy: (1) They are extremely dirty, causing severe cleanup and corrosion problems; (2) they have poor deliverability; and (3) they can cause permanent electrical problems when applied in aircraft interiors.

E. HALONS

Halons are halogenated hydrocarbons which extinguish fires by disruption of free-radical chain reactions. Many halocarbons have been used as fire suppressants (Reference 34); however, by far the most common at present (in order of decreasing use) are bromotrifluoromethane (CF_3Br, Halon

16

1301), bromochlorodifluoromethane (CF_2BrCl, Halon 1211), **and** dibromotetrafluoro-ethane (CF_2BrCF_2Br, Halon 2402). On a volume basis as gases, the order of increasing extinguishing ability for premixed flames is Halon 1211 < Halon 1301 < Halon 2402 (Reference 35). Extensive evaluations of halon agents have been reported (Reference 36).

It has been stated that "fire extinguishing agents also are activated in [fires] and perform in ways that at times are not apparent" (Reference 2). In a three-dimensional fire scenario (Reference 1) halons seem to extinguish high-temperature fires better than low-temperature fires.[*] The fire itself activates the halons. When halon agents enter a fire the initial reactions may be thermal or chemical. For Halon 1301, flame composition studies indicate a chemical decomposition (Reference 37); the principal initiating reaction is apparently hydrogen atom abstraction of a bromine atom (Reference 38).

$$CF_3Br + H \rightarrow HBr + CF_3 \tag{21}$$

This reaction is exothermic ($\Delta H_{298} = -18.1$ kcal/mol).

The next reaction step in suppression of hydrocarbon fires also exothermic ($\Delta H_{298} = -16.6$ kcal/mol):

$$HBr + H \rightarrow H_2 + Br \tag{22}$$

The net reaction of these two steps is the formation of diatomic hydrogen, a relatively unreactive species (Reference 39) owing to its very high bond energy of 104 kcal/mol. Hydrogen atoms (and other monoatomic species)

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[*]Harold D. Beeson, New Mexico Engineering Research Institute, private communication. In work performed under contract F29601-84-C-0080 on three-dimensional fire extinguishment, times to extinguishment tended to decrease with increasing flame temperature. This observation was not included in the final report on this project (Reference 1) because of insufficient data.

cannot combine directly without the involvement of a third species, M (nitrogen, oxygen, argon, particulate carbon, container walls).

$$H + H + M \rightarrow H_2 + M \tag{23}$$

A third body is needed to carry off the energy evolved in bond formation. Since three-body collisions are rare, hydrogen atoms combine slowly in flames. Halon molecules provide a facile pathway for combining hydrogen atom, thereby, removing these highly reactive, chain-propagating species.

The mechanism outlined above emphasizes the importance of the hydrogen atom in inhibition reactions, an importance found in other reaction models (Reference 40). Hydroxyl free radicals can also be deactivated by halon-produced hydrogen bromide.

$$OH + HBr \rightarrow Br + H_2O \tag{24}$$

This reaction is highly exothermic ($\Delta H_{298} = -31.8$ kcal/mol) but plays a less important role than does the reaction presented in Equation (22) in suppression of fires (Reference 41).

Halons exhibit three important features. First, they are clean agents. They do not interfere with Navy or Air Force readiness. No cleanup is necessary and, in the absence of structural damage, aircraft and other equipment can be used as soon as a fire is extinguished. Second, halons are highly effective. Concentrations of only a few percent are necessary to effect extinguishment. Third, halons do not interfere with electrical operations. They can be used in aircraft interiors.

Halons do have several drawbacks, some of which are serious. Halons are toxic, and the better halon agents are often the most toxic (Reference 42). Because of their increased effectiveness, however, halons are often less toxic than carbon dioxide when the concentrations of both are sufficient for fire extinguishment. Gaseous halons have very poor

18

deliverability in outdoor applications, and they do not give good security with liquid fuels. Finally, recent studies indicate that halons may have a significant impact on stratospheric ozone (Reference 43). Halons are estimated to be up to 10 times more effective than chlorofluorocarbons in decomposing ozone (Reference 44). Owing to its chemical structure, Halon 1211, a major agent in aircraft protection, is believed to pose a greater environmental threat than Halon 1301 (Reference 45).

SECTION V
RATIONALE

Criteria for an Air Force/Navy agent must include the following:

1. To ensure readiness, the agent must be clean. Undamaged aircraft in or near a fire extinguishment operation must be immediately available for use. Excessive manpower must not be diverted to cleanup detail following a fire, particularly during wartime. Electrical components must remain usable.

2. The agent must have an acceptable toxicity and environmental impact. High health and environmental risks seriously affect agent usefulness.

3. The agent must have good deliverability. For streaming applications, this precludes gases. New application methods, now under development, may allow delivery of gaseous agents.

4. The agent must be able to secure a fuel against flashback.

5. The agent must have a good dimensionality.

Halons and related agents offer the best prospects for satisfying these requirements. They are the only truly effective, three dimensional, clean agents known today. Halons have, however, major drawbacks in toxicity, security, and deliverability. The following proposed work emphasizes halons and halon-like suppressants that act through chemical mechanisms.

SECTION VI

HYPOTHESES

A. IODINE COMPOUNDS

The effectiveness of halogen substitutents in halons increases in the order F < Cl < Br < I (Reference 46). By assigning values of 1, 2, 10, and 16 to fluorine, chlorine, bromine, and iodine (Reference 47), one can score halons and arrive at excellent predictions of their relative extinguishing capabilities (Reference 46). Unfortunately, iodine compounds, the most effective halocarbon agents, are often toxic. They are good methylating compounds and are, therefore, suspect carcinogens.

Higher molecular weight alkyl iodides, particularly oils and partial polymers, may have acceptable toxicities. The higher molecular weight compounds will offer improved fuel-securing properties. Organic iodides must receive careful consideration as suppressants.

B. SYNERGISTIC MIXTURES

Synergism is a mutual enhancement of the activities of two substances so that a mixture has better properties than either component. The use of free-radical initiators for synergistic enhancement of halogenated fire extinguishants has shown no synergism (Reference 48); however, other possibilities exist and some of these are discussed below.

Studies indicate that a mixture of Halon 1211 and Halon 1301 is a better extinguishing agent than either pure halon when applied separately (Reference 49). Owing to fire size (1 ft^2) these results are suspect; however, other testing at Tinker Air Force Base has given similar results. Laboratory-scale experiments using a diffusion flame do not show a mixture to be better than the separate agents; however, they do show a dramatic improvement in extinguishing ability of Halon 1211 with small amounts of

added Halon 1301 (Appendix A). These latter results indicate that the effect may be molecular.

Creitz (Reference 50) has shown that inhibition is much greater when halon suppressants are added to the oxygen side of diffusion flames. The inhibition becomes particularly great when oxygen is deficient. Thus, combinations of halons with materials causing oxygen depletion may be synergistic. One such material could be additional fuel. Hydrocarbons normally considered as fuels (methane, butane, ethylene, butadiene) are exceedingly strong inhibitors of hydrogen-air flames (Reference 51). With the saturated hydrocarbons this effect is probably due to hydrogen abstraction.

$$H + CH_4 \rightarrow H_2 + CH_3 \tag{25}$$

For unsaturated hydrocarbons, hydrogen atoms may add to the double bond.

$$H_2C{=}CH_2 + H \rightarrow C_2H_5 \tag{26}$$

The radicals formed by this process are less reactive than the hydrogen atoms from which they are derived. Unsaturated alkyl halides could act as highly effective extinguishing agents. A fuel source giving rise to oxygen depletion could be built into the inhibiting molecule. In addition to oxygen depletion, a fuel source could also provide the heat necessary for proper utilization of halons such as Halon 2402, for which thermal decomposition pathways are important. Serious practical and safety problems would have to be overcome in approaches of this type.

C.   INITIAL REACTIONS

The initial reactions which halons undergo upon entering a flame front are uncertain. Free-radical abstraction is involved, but pyrolysis plays a part. Molecules containing bromine atoms can be designed to be susceptible to thermal degradation. Such molecules should enter into reaction faster

and with lower losses. It has been estimated that, even under the best of situations, only 5 percent of the halon applied to a fire participates in suppression. The remaining material is lost. Molecules designed to participate more readily in the initial reactions could give up to a 20-fold increase in suppression capability.

To investigate these designed molecular agents, laser Raman spectroscopy is needed to examine the molecules as they enter a flame front.

D. SUBSTITUTED HALONS

A number of halon modifications may offer significant improvements in action. Recent work at the University of New Mexico toxicology laboratory indicates that the addition of a methoxy group to a halogenated hydrocarbon significantly decreases its anesthetic properties. Toxicologists have long recognized that, for a homologous series of compounds, toxicity decreases with polarity. Modification of halons by addition of substituent groups may significantly improve toxicity without sacrificing extinguishment capabilities. Increase in molecular polarity may also improve the securing capabilities since vapor pressure decreases with increasing polarity.

SECTION VII
RESEARCH PLAN

A.   LABORATORY STUDIES

Work with a cup burner and small pan fires will continue. These permit
a rapid evaluation of the efficacy of an agent. Careful consideration will
be given to agent properties to avoid testing materials which could not be
incorporated into the Air Force and Navy system owing to toxicity, poor
deliverability, or expense. Testing of the following classes of agents are
planned.

1.   Iodinated organics with an emphasis on high molecular weight
materials.

2.   Halogenated unsaturated hydrocarbons.

3.   Mixtures of halons with hydrocarbon fuels. Although this appears
to be impractical, such a mixture could be noncombustible and a highly
effective agent.

4.   Halons with methoxy and other polar substituents.

5.   Thermally degradable halons.

B.   LASER RAMAN SPECTRAL STUDIES

The work proposed herein is designed to further elucidate the action of
halocarbon fire suppressants (halons) when introduced into a burning system.
The main goal of the work is to develop new agents from the information
obtained. The most important information is the characterization of the
initial reactions of halons as they enter a fire. The experiments have been
designed to characterize radical formation as halons enter the preheat or
induction zones of flames. The experiments will determine how halons

initially fragment to form radicals or ions that quench flames. The results will give an understanding of halon action and are essential in the design of more effective fire suppressants.

Previous work carried out in these laboratories has consisted mainly of pyrolysis studies involving halons, especially Halon 2402. A data base showing the products formed under various conditions of halon pyrolysis has been generated. These studies have established the spectral characteristics of many of the halon products that might be formed in a fire and data obtained can be used in the characterization of an actual flame system to which a halon has been added. The results only indicate equilibrium data, however, and will not contribute greatly to the characterization of the initial radical-forming reactions that will be probed in the present studies. The study of the pyrolysis products revealed that the Raman technique appears to be exceedingly sensitive. It will be possible to detect very small quantities of molecules, ions, and radicals in the flame system.

Present studies are being expanded. A burner has been designed and constructed to produce a flame ideal for the studies planned. Details of the burner system and the flame that it will produce are discussed below. The general design characteristic has been, however, to keep the flame as simple as possible. With this in mind, the flame is designed to be pseudo-one-dimensional and to show distinct spatial zones. Thus, with Raman spectroscopy, it will be possible to optically probe very small regions of the flame and spatially characterize radical and molecule distributions. This will allow a comparison of the results obtained with theoretical models that have been developed for simple flames. These models have contributed greatly to the understanding of such systems, but have not been tested in an analytical flame. The ability to characterize the results that will be produced with these theoretical models is an important facet of the work proposed here.

Many factors have been considered in the overall burner design. The most important criterion is that the flame exhibit distinct zones, including the preheat zone, the primary reaction zone, and the mantle region. In the preheat zone the gases begin to heat by conduction and radiation. It is necessary to determine whether the halon fire suppressants begin decomposition in this region. The primary reaction zone is characterized by high radical concentrations and nonequilibrium. Most of the primary flame reactions occur within this zone. This zone must be distinctly defined so that it can be optically probed. In the region above this zone, the mantle region, the flame is characterized by equilibrium concentrations of molecules and radicals. Since this region extends for several centimeters above the primary reaction zone, it is the most easily characterized zone. To produce a flame with well-defined zones, premixed gases and a highly laminar flow are necessary. It is also desirable to shield the flame from the ambient atmosphere, eliminating the introduction of additional oxygen and decreasing flame turbulence. This can be achieved by building a shield burner constructed from a quartz-like material, or by surrounding the flame with a laminar flow of dense, inert gas. Argon has been chosen as the shield gas.

The initial work will involve the use of an oxygen/hydrogen flame. These gases were chosen because they give the simplest system, and the flame is the most susceptible to theoretical modeling. Indeed, the models for oxyhydrogen flames are probably more accurate than those for any other flame. Another factor in the choice of oxyhydrogen is that the flame background is extremely low level. This characteristic allows the measurements of the intermediate species to be performed with great sensitivity. A complication of studying any flame is that a premix burner must be used if a stable, nonturbulent flame is to be produced. The burning velocity of oxygen/hydrogen mixtures is extremely high; burner flashback can easily occur. The burner must be very carefully designed to eliminate the possibility of flashback.

A slot burner configuration was chosen. The slot consists of a very narrow slit, 2 centimeters long. This configuration allows the production of a pseudo-one-dimensional flame. One can optically probe approximately 1 centimeter in the center of the flame and avoid the ends, where there might be some interaction with the surrounding atmosphere. In addition, the ability to image a 1-centimeter region of the flame onto the entrance slit of the spectrometer will allow the collection of much more light than if a point in the flame were imaged. The burner itself consists of the actual burner head, a gas-mixing region, and a support system to hold the burner in place on the optical table. Engineering drawings of the burner system have been prepared. The burner design allows for interchanging burner heads so that slots of different dimensions can be used. This will allow the expansion of these studies to the combustion of gases other than oxygen and hydrogen. In addition, the burner head is designed so that the argon sheath slots can be moved to place the sheath in an optimal position for the particular type of flame being studied. Finally, the burner head incorporates water cooling to prevent it from overheating, and, more importantly, to keep it and the gases flowing through it at a constant temperature. This will establish a more reproducible flame and will result in a more accurate characterization.

The dimensions of the slots on the burner head are very important. The length of the slot, 2 centimeters, was chosen to match the optical requirements. The width and the depth of the slots, however, were chosen to achieve laminar flow. The Reynolds number, R, of a flowing gas can be calculated from Equation (27).

$$R = \frac{VD}{a} \tag{27}$$

where V is the average velocity of the gas, a is the viscosity of the gas divided by its density, and D is the diameter of the hole through which the gas is flowing. In the case of a slot burner,

$$D = \frac{2LB}{L + B} \tag{28}$$

where L and B are the length and width of the slot respectively. For L >> B, D is approximately equal to 2B. To achieve a highly laminar flow the Reynolds number must be less than or equal to 2300. The burning velocity of an oxyhydrogen flame is approximately 4000 cm/s; thus, it is necessary to have a very high gas velocity through the slot. The dimensions of the burner slot were chosen to be 3 centimeters deep and 0.04 centimeters wide. With these dimensions, Equation (27) predicts that the flow will be highly laminar for a wide variety of gas velocities through the slot. The same considerations were given to the dimensions of the sheath slots, where a highly laminar flow of argon is desirable.

The burner slot is fed by a flow of gas from the mixing chamber. The mixing region was designed to contain the smallest possible volume of gas. Thus, if flashback into the mixing chamber does occur, only a minor explosion will result. The chamber must, however, be large enough to allow thorough mixing of the fuel, oxidant, and any other gas added through the third port. It is through this third port that the halon fire suppressant will be added to the flame. Some of the initial studies will involve the introduction of Halon 2402. Because Halon 2402 is a liquid at room temperature, it must be heated prior to introduction. Owing to the relatively low boiling point of 47 ^{o}C, Halon 2402 has a significant vapor pressure and can be vaporized without having to operate at high temperatures.

Much of the work underway at the present time involves installation of the burner into the Raman instrument, as well as modifications to the apparatus and the laboratory to allow operation of the flame system. The two areas of modification are:

1. An exhaust system has been constructed. An extension of the fume hood from an adjacent laboratory into the area of the Raman apparatus has been accomplished. The flame will be exhausted directly into this fume hood extension, and thus will allow safe operation. It is important that the

28

combustion products, such as fluorinated or brominated gases, not be allowed to enter the room air supply.

2. The Raman instrument optics must be reconfigured to allow for optimal imaging of the flame system. The initial modifications involve only adjustment and realignment of the optics to position the burner so that the flame is in the laser beam. This is necessary because the top of the burner is a significant distance off the optical table when compared to the earlier studies involving halon pyrolysis products. The optical transfer system is designed to transfer the image of a 1-centimeter region of the flame onto the entrance slit of the spectrometer.

Once the burner has been installed and some initial characterization has been performed, additional modifications will be accomplished. Two optical tricks will be used to produce measurements as sensitive as possible. First, a concave mirror will be placed on the far side of the flame from the monochromator slit. The focal length of the mirror has been chosen so that radiation emanating from the flame and striking the mirror will be focused onto the monochromator slit. This should effectively double the amount of Raman scattering collected at the slit. The amount of Raman scattering can also be increased by using a system to multipass the laser beam through the flame; however, such a system decreases spatial resolution. The mirror can be placed behind the flame and the laser beam can be directed to make two passes through exactly the same region. This will effectively double the laser scattering without degrading the spatial resolution achieved.

Proper system alignment is critical, and a significant effort will go into optimizing the entire system alignment. Once the system has been optimized, it is expected that halons can be measured within the flame at pressures as low as 1 torr, a conservative estimate based on the pyrolysis studies. The system will be exceedingly sensitive and will allow for a very precise and highly spatially resolved imaging system.

One of the burner design features discussed above is formation of a pseudo-one-dimensional flame, that is very narrow and relatively long. Thus, the central portion of the flame will be uniform. The flame will propagate against the flow of gases coming out of the burner head. As one moves off the burner in height, a time axis, relative to the gas velocity, describing processes in the flame, will be established. All measurements will be relative to distance above the burner head (time). Measurements of a concentration or temperature profile will be functions of height.

A first step in the measurement of flame properties is the establishment of a temperature profile of the oxyhydrogen flame. Temperature profiles can be measured in a number of ways, using Raman spectroscopy. An outline of the measurement process to be attempted here is discussed below.

Raman spectroscopy is a scattering technique and the phenomena that can be observed when monochromatic light is scattered by a molecule must be considered. The predominant scattering mechanism is Rayleigh scattering, where the scattering light has the same energy as the incident beam. Two other types of scattering occur where the scattered beam has a spectrum of energies that reflect the difference between the energy of the monochromatic probe beam and the vibrational energies of the scattering molecule. If the scattered radiation represents the energy of the probe beam minus the vibrational energies of the molecule, it is termed "Stokes scattering." If the scattered radiation is made up of the energy of the probe beam plus the vibrational energies of the molecules, it is called "anti-Stokes scattering." The use of the distribution of intensities within the Raman scattering phenomenon allows calculation of the temperature of the molecules from which the light is scattered.

Stokes scattering involves transitions from lower vibronic states to the next higher vibrational states; anti-Stokes scattering involves transitions from an upper vibronic states to the next lower states. If a molecular system is in equilibrium, the Boltzmann population distribution

predicts that the ground-state population will be much greater than the population of any of the excited states. The population in the excited states decays exponentially as the energy of the excited states is increased. Equation (29) gives the Boltzmann population distribution between the excited state, N_1, and the ground state, N_o,

$$\frac{N_1}{N_o} = e^{-\Delta E/kT} \qquad (29)$$

where ΔE is the difference in energy between the two states, k is the Boltzmann constant, and T is the absolute temperature. Temperature measurements using Raman spectroscopy are obtained by relating intensities of transitions from various states to the populations within those states. To do so one must know transition probabilities from one state to the other and have some means of accurately measuring relative or absolute intensities. Fortunately, for the molecules of interest in this study (O_2, OH, and H_2O), the transition probabilities from state to state are relatively well-characterized.

The simplest method of making a temperature measurement based on Raman scattering is to measure the intensity of a transition between the same states in both the anti-Stokes-Raman spectrum and Stokes-Raman spectrum. This method is appealing because the transition probabilities between the two states cancel and only the population ratio remains. The Stokes and anti-Stokes transitions are, however, separated by as much as 1000 wave numbers. This feature makes it nearly impossible to accurately measure relative intensities unless the entire optical system has been carefully calibrated against a well-known intensity standard. This is both difficult and expensive.

Another method of temperature measurement uses the Stokes spectrum to calculate the flame temperature. In this method, population ratios are again used. Because of the anharmonicity of the vibrational energy well, Raman spectra of the excited states will produce peaks separated by as much

31

as 6-10 wave numbers. Examples of known Stokes spectra of N_2 and O_2 in a flame can be found in Reference 52. This degree of separation is easily measurable with the optical system used in these studies. A 6-10 wave number separation is sufficiently close in energy so that one can assume the grating and detector efficiencies to be constant. Indeed, this assumption has been shown to be good to better than 1 percent. Thus, the intensity of the peaks can be measured and directly compared so that accurate intensity ratios for the transitions from state to state can be measured. From the transition probabilities for the specific transitions, a population distribution can be determined and Equation (29) can be employed to calculate an absolute temperature. Temperature measurements made in this manner can be relatively accurate. The highest uncertainty in the measurement is associated with the transition probabilities. This is not a major problem, however, because most of the studies to be performed will be relative to one another. Thus, even though the temperatures might not be entirely accurate on an absolute scale, differences seen from experiment to experiment will be valid.

Another background study that will be performed will be to characterize concentration profiles of all important species within the flame. Raman spectroscopy is sensitive to centrosymmetric diatomic molecules (O_2, H_2, N_2, etc.) as well as to noncentrosymmetric diatomic and polyatomic species. Thus, all species present are characterizable. Measurement of absolute concentrations of species from Raman spectroscopy is an extremely difficult process for which the entire optical system must be precisely and absolutely calibrated. Furthermore, such measurements depend upon poorly characterized constants such as scattering cross sections. On the other hand, it is relatively easy to measure relative concentrations of species within the flame. The intensity of scattering as a function of position in the flame, if all other variables are held constant, is directly related to concentration changes. Thus, it is straightforward to develop relative concentration profiles of all important species. This will be an important step in the overall process of flame characterization.

Once the background characterization has been completed, halons will be vaporized, fed into the mixing chamber of the burner, and introduced, along with the support gases, to the flame. The concentrations of the halons will be varied, but kept in a range below that needed for extinguishment. Raman spectra will be taken as functions of halon concentration throughout the different regions of the flame. The initial studies will focus on the preheat zone to answer the question of whether or not the halon decomposes before it enters the reaction zone. If it does decompose, the products formed will be of interest.

Characterization of the primary reaction zone of the flame is expected to be complicated. Much of the effort in the design and planning of experiments to be carried out in the coming year have been done to minimize these complications. The pseudo-one-dimensional flame system should show no problem with flame regions mixing. This characteristic eliminates the uncertainty that would be introduced by having more than one region being imaged onto the spectrometer at one time. This will help minimize the number of species that are within the scattering region of the laser beam. The use of an oxyhydrogen flame will keep the number of scattering species to a minimum, and those that are present will be relatively easily characterized.

Identification of some unknown spectra will have to be accomplished. The identification will be performed in one of two ways. The Raman library of flame species and pyrolysis products, already partially developed, is being used to develop computer routines to scale and subtract known spectra from unknown spectra. In this manner one can strip a spectrum down to a minimum number of unidentified peaks so that unknown species can be more easily identified. The second method of unknown identification will be to use normal-mode analysis to assign Raman peaks to species that could be present in the flame. For the unstable radicals that would be present for only a short duration in the flame, there will be no library spectrum; these species are not be present in an equilibrium mixture following a pyrolysis experiment. On the other hand, once a species has been identified by

normal-mode analysis and a spectrum for it has been stored, one can easily, via computer methods, identify these species in future experiments and subtract their spectra from the unknown. It is expected that the only unknowns encountered will be those due to the breakdown of the halons and products formed from reactions between these breakdown products and gas constituents. This fairly limited spectrum of possible species will be manageable and identification will be complete.

Once the unknown spectra have been identified it will be necessary to map concentrations of known gas reactants within the flame. These concentration maps will be compared to the maps developed with no halon present. It will be important to see how the concentration profiles shift. It is expected that the radical quenching mechanisms arising as a result of halon addition will dramatically shift the concentration profiles of some of the important flame gas reactants.

The flame itself will be operated under a variety of conditions to answer questions about halon/flame interactions: Is there an observable difference between reducing and oxidizing flames? How does the performance of a halon compare in flames of different character? Do the radical species change with a change in the flame character? These and other questions should be easily answered once the entire system is operational and the initial flame systems have been characterized.

Following system and library establishment, the studies should be straightforward and proceed at a rapid rate. A significant effort will be spent in the early stages of the experimentation. Several experiments will have to be performed to completely characterize the oxyhydrogen flame and the performance of the first halocarbon introduced. Once this is accomplished, however, it will be relatively easy to extend the studies to other halons. These studies should progress rapidly. Only the identification of the unknown halon decomposition products will have to be accomplished. The results should allow differences between performances of various halons to be easily compared. Indeed, one should be able to develop

a quantitative measure of halon performance relative to its radical
quenching properties within a given flame system.

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APPENDIX A

CUP BURNER TESTS OF HALON 1211/1301 MIXTURES

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CUP BURNER TESTS OF HALON 1211/1301 MIXTURES

The following tests were conducted to compare combination Halon 1301 and Halon 1211 agents with 100 percent 1301 or 1211 in suppression of small scale controlled flames. Combination 1211/1301 extinguishers are currently on the market. The combination agents tested contained 25, 50, and 75 percent Halon 1301 by volume.

A. APPARATUS

Flame-extinguishing concentrations of the halons were measured with a standard cup burner (Hirst, R. and Booth, K., "Measurement of Flame-extinguishing Concentrations," Fire Technology, Vol. 13, pp. 296-315, November 1977) in a flowing atmosphere. A 28-millimeter diameter cup used for the burner was mounted to a glass tube allowing fuel to flow to the cup. The total length of the burner cup was 340 millimeters. The burner was mounted on the axis of a 85-millimeter diameter glass chimney 760 millimeters in length. The surface of the fuel in the cup was 310 millimeters above a layer of glass beads. A mixture of air and agent passed through the layer of beads and flowed past the burner cup. The fuel cup was far enough above the glass beads to inhibit any disturbances in the flow. The flame for each test was uniform and smooth.

The flow of the air and the agent were measured with separate flow-meters. The air and halons were combined in a T-connector, with final mixing occurring in the layer of glass beads. A reservoir of fuel was connected to the burner cup stem by a piece of flexible tubing. The reservoir could be moved up or down to maintain an exact fuel level in the burner cup.

B. METHOD

A 10-second preburn was allowed for each test. Any longer period might have caused the fuel to reach its boiling point. This would require a higher concentration of halon to extinguish the flame. The fuel level was maintained at 2 millimeters below the lip of the fuel cup to prevent any spills from the ignited fuel. The concentration of halon was increased in the airflow until the flame was extinguished. The temperature of the air was monitored for each test from a thermocouple inserted in the tubing coming off of the air flowmeter. A period of 10 seconds between each increase in the halon concentration was allowed for the agent to flow from the meter to the burner. Airflow to the chimney was kept at a constant 40 L/min for each test. The initial halon concentrations were started at approximately 2 percent, and then were increased by approximately 0.1 percent every 10 seconds until the fire was extinguished.

The two agents were mixed by placing a given weight of Halon 1301 in a stainless steel container through a high-pressure hose. The valve on the cylinder was closed and the pressure hose was removed. The cylinder was placed in a liquid-nitrogen bath to keep the Halon 1301 below its boiling point. A beaker was cooled in another liquid nitrogen bath to contain the Halon 1211. The valve on the cylinder was removed and the exact amount of Halon 1211 was added to produce the correct mixture ratio. All mixtures were produced by weight.

JP-4 jet fuel was used in the extinguishment tests. Two tests were run on the 100 percent Halon 1301 and 100 percent Halon 1211. Three tests were conducted for each combination agent. The results were averaged for each halon or halon mixture to obtain the extinguishment concentration. Since the vapor pressure of Halon 1301 is higher than that of Halon 1211 there could be a higher percentage of Halon 1301 flowing to the chimney than was actually in the mixture. To find if this occurred and to see how well the two agents were mixed, two tests were run with the agent container upside down. This permitted the drawing of only the liquid form of the mixture. Both agents vaporized before reaching the flow meters. A third test was run with the bottle correct side up. In this test only the vapor head off the liquid mixture was drawn. The test results from the two container positions showed little or no difference for extinguishment of the flame. This observation shows that in these tests, the higher vapor pressure of Halon 1301 does not significantly enhance its concentration in the gas reaching the burner.

C. RESULTS

The test results shown in Table A-1 indicate that Halon 1211 requires the highest concentration to extinguish the flame, whereas the 100 percent Halon 1301 and the 75 percent 1301/25 percent 1211 require the lowest concentration. There appears to be an anomalously large increase in extinguishing power for small additions of Halon 1301 to Halon 1211. Owing to the relatively large standard deviations, additional tests are planned.

TABLE A-1.   INITIAL RESULTS OF CUP BURNER TESTS ON HALON 1211/1301 MIXTURES

Agent	Test	Agent state as ejected	Extinguishment, %
100% 1301	1	gas	2.44
	2	gas	2.44
	average		2.44
100% 1211	3	gas	2.61
	4	gas	2.61
	average		2.61
25% 1301/75% 1211	5	liquid	2.45
	6	liquid	2.44
	7	gas	2.46
	average		2.45
50% 1301/50% 1211	8	liquid	2.54
	9	liquid	2.54
	10	gas	2.46
	average		2.50
75% 1301/25% 1211	11	liquid	2.41
	12	liquid	2.46
	13	gas	2.41
	average		2.43

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